ERG No. 0195.00.002
TECQ Contract No. 582-04-65589
Work Order No. 05-06

ASSESSMENT OF NOₓ EMISSIONS REDUCTION STRATEGIES FOR CEMENT KILNS - ELLIS COUNTY

DRAFT EXECUTIVE SUMMARY

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This study is the work project of a panel of experts assembled at the request of the Texas Commission on Environmental Quality. This study was performed under contract to Eastern Research Group that provided overall contract management and subcontracted the outside experts and laboratory services. While each of the experts brought specific skills to this study and was the principal author of individual sections of the report, the overall study represents a team effort. The general conclusions of the study have been reviewed and are endorsed by the entire expert panel.

Signed_____

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1.0 INTRODUCTION

This study was conducted to explore potential NO_x emissions reduction strategies for cement kilns in Ellis County. This project included assessing existing NO_x control technologies as well as new technologies that have not been previously considered by TCEQ. This project evaluated the general performance and cost of applicable NO_x control technologies for the cement kilns present in Ellis County and further evaluated the application of these control technologies to the site-specific requirements of the kilns and raw materials present in Ellis County.

This study was initiated in order to fulfill obligations in the Dallas/Fort Worth Litigation Settlement Agreement. TCEQ, in consultation with the Plaintiffs, EPA, and Intervenor the Portland Cement Association, developed the scope of work and selected Eastern Research Group (ERG) and a panel of experts (the ERG Team) to perform this cement kiln NO_x control technologies study. This study evaluated the applicability of existing control technologies and the potential availability of new air pollution control technologies for cement kilns located in the Dallas/Ft Worth ozone nonattainment area. This report evaluates and establishes type of controls that may be technically applied to the three nonattainment area cement plants with specific evaluations of applicability to the 10 cement kilns located at the three plants. This report focuses largely on three active types of control technology: SCR, SNCR and NO_x Oxidation. This focus in based on the need to evaluate technologies that go beyond current requirements of TAC Chapter 117. Economics of these control technologies are also investigated and reported.

The intent of this study was to establish impartial parameters for the determination of applicable controls. Controls were included to the extent that they were technically feasible. Control costs and cost effectiveness values, in terms of cost per ton of NO_x controlled, were then assigned to all technically feasible controls. The ERG Team has not applied value judgments or assessed the economic viability of technically feasible controls. The ERG Team has not excluded control technology on the basis of cost. This study puts forward technically viable NO_x control technologies and evaluates their cost effectiveness for specific application to Ellis County cement kilns with the intent of allowing TCEQ and other interested parties to have sufficient information make control technology selections.

This report uses the USEPA report "NO_x Control Technologies for the Cement Industry" of September 2000 (EPA 2000) as a baseline for the technical analysis and as boilerplate for

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describing the cement industry and applicable control technologies. The ERG Team has reviewed and edited this text to reflect the Team's understanding of the processes and control techniques. As mentioned previously, this report looks at active control technologies beyond the combustion and process optimization techniques of TAC Chapter 117. The EPA 2000 report evaluates Selective Catalytic Reduction (SCR) and Selective Non-catalytic Reduction (SNCR) for the cement industry. This study takes this EPA 2000 information and updates it to the present. In addition, this study conducts site-specific evaluations including control cost evaluations for the 10 Ellis County cement kilns. This study focuses on application of SCR, SNCR and oxidation technologies including LoTOx to control oxides of nitrogen. Energy improvements are also examined, including the replacement of the seven Ellis County wet kilns with two large, modern dry process units.

1.1. EXECUTIVE SUMMARY

The tables presented below contain summaries of control technology evaluations conducted as part of this study. The summaries below generally contain conservative costs and scenarios for the selected technologies. For example, performance levels for selective catalytic reduction (SCR) and LoTox oxidation are conservatively estimated at 80-85%. These technologies typically perform better than these levels in other industrial applications. However, using a slightly lower performance value presents a more conservative evaluation of control costs allowing potentially difficulties in initial application of these technologies to Ellis County cement kilns.

The tables include a column discussing the status of the control technology for the application. This column uses the Top-Down BACT terms, *available, transferable* and *innovative*, to describe the status of the control technologies. However, for the purposes of this presentation, *available* essentially means that the technology is commercially available and in use on the similar types of cement kilns. *Transferable* means that the technology is commercially available an in use on similar process equipment and could reasonably be expected to work on they type of cement kiln. *Innovative* describes technologies that have not been successfully applied to a type of cement kiln, but in the judgment of the ERG Team could be expected to work on the type of cement kiln if correctly optimized through experimental application.

Using these definitions for control status, no control technology is *available* for wet kilns and only *transferable* or *innovative* controls are proposed. Wet kilns use more energy and have higher emissions rates than dry kilns. The only *available* wet kiln option evaluated in this study is conversion of the wet kilns to modern dry preheater/calciner units. This is a high cost alternative with a cost of approximately $11 per metric tonne (the metric tonne is the standard unit of measure for cement production and is used in this report) of clinker produced including consideration of substantial reductions fuel savings due to increased efficiency. As the cost of alternative controls approaches this value, there is reasonably expected to be a point where the cost of control technologies may create a substantial incentive to replace the wet kilns. This decision is complex and may require consideration of expanded production and use of alternative

energy sources to be commercially justified. Burden costs in $/tonne of clinker are provided to provide insight into the impacts of control costs on the cement plant's cost of product. The emissions reductions calculated in Tables 1-1 through 1-8 are based on operation of the control equipment for the entire year and not just during the Dallas/Ft. Worth ozone season.

1.1.1. Control Alternatives for Holcim Inc.

Holcim operates two modern dry preheat precalcination kilns each with an annual production capability of slightly over one million tons per year of clinker. Holcim has recently completed testing of SNCR on these kilns. SNCR performed reasonably well on Holcim #1, but additional optimization may improve performance.

Holcim #1

Holcim's Line #1 began operation in 1987. While essentially a modern design, typical of units built in the 1980's, and may be a candidate for a reconstructed preheater precalcination tower to a larger, more energy efficient design (see Section 4.4.5 of the report). This reconstruction could also allow for improved staging of combustion, lower NO_x generation and improved integration with controls such as SNCR or an oxidation control technology. Without modification, Holcim #1 will likely achieve somewhat lower control performance than Holcim #2 or TXI #5 based on application of similar technologies. However, in spite of it's older generation of design, Holcim #1 is currently performing nearly as well as Holcim #2. Neither Holcim #1 nor Holcim #2 is currently performing as well as TXI #5 in terms of energy efficiency or NO_x emissions rates.

Note on the conventions used in the Tables 1-1 through 1-16.

The metric tonne (1,000 kgs. or 2,205 lbs.) is used by the cement industry for measuring and reporting production. Emissions are reported in short tons containing 2,000 lbs./ton. This results in a 10% difference between the metric tonne and the short ton. A controlled emissions rate of 1.1 lbs./tonne is equivalent to a controlled emissions rate of 1.0 lbs./ton. Emissions reported in tpy are in short tons per year.

Table 1-1 Summary of Technologies for Holcim #1 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Available	2,222	3.76	85%	1,888.7	0.56	$1,700	$2.70
LoTOx	Transferable	2,222	3.76	85%	1,888.7	0.56	$2,200	$3.50
SNCR	Available	2,222	3.76	50%	1,111	1.9	$1,400	$1.30
Calciner Upgrade	Available	2,222	3.76	40%	888.8	2.2	$2,795	$2.70

40% for new low-NOx calciner based on literature.
Cost effectiveness for calciner upgrade calculated by ratio of burden costs using SCR data.

Holcim #2

Holcim's Line #2 began operation in 1999. Holcim #2 is a modern design, but emits substantially more NO$_x$ than TXI #5 that was built only two years later. There may be process or combustion optimization options for Holcim #2 that can lower NO$_x$ prior to control. Holcim has recently completed testing of SNCR on these kilns. SNCR did not perform as well as would be expected on Holcim #2 and additional optimization should improve performance.

Table 1-2 Summary of Technologies for Holcim #2 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy.	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Available	1,778	3.01	85%	1,511.3	0.45	$1,700	$2.20
LoTOx	Transferable	1,778	3.01	85%	1,511.3	0.45	$2,100	$2.80
SNCR	Available	1,778	3.01	50%	889	1.5	$1,600	$1.20

1.1.2. Control Alternatives for TXI Cement

TXI operates five kilns, one modern dry preheat precalcination kiln and four 1960's era wet kilns. Two of the wet kilns are operated full time and two are operated as backup units about 15% of the time.

TXI #1 and #4

TXI #1 began operation in 1960 and TXI #4 began operation in 1972. These are wet kilns that use the old process of making cement from wet slurry. This makes high quality cement but uses substantially more energy to make cement. Both energy use and NO_x emissions rates are substantially higher for wet kilns than for dry process kilns. Because the kilns are of similar size and used in a similar manner, one estimate has been created to represent both TXI #1 and TXI #4. Cost and control estimates are based on averaging the operation of these kilns; a similar approach has been used for TXI #2 and #3. A control option for replacement of the wet kilns at TXI with a new large dry kiln of equal capacity to the old wet kilns is also presented. The model for wet to dry conversion contains a calculation for fuel savings that is not entirely accurate for TXI because of the use of waste fuels in the wet kilns. However, to the extent that a new, larger dry kiln would continue to utilize a similar amount of waste fuels, the savings in fuel expressed as coal would still provide an accurate view of a potential fuel savings. The models for TXI #1 and #4 presume that mid-kiln firing will be applied as required under the current SIP and that this will achieve a 30% reduction in NO_x emissions. This 30% assumption is based on evaluation of literature and other installations and is not intended to predict the actual ability of TXI to reduce emissions through mid-kiln firing.

Assuming mid-kiln firing reduces the emissions rate from current actual rates and decreases control cost effectiveness. As less NO_x is available for control, the cost per ton controlled is increased. However, as mid-kiln firing is already required under Texas regulations, this was deemed the proper starting place for control analysis. The analyses for TXI #1 and #4 presented below are based on an average for the two kiln and values presented below, such as emissions reductions, should be doubled to account for both kilns.

Table 1-3 Summary of Technologies for TXI #1 & #4 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNOx/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNOx/tonne	Cost Effectiveness $/ton NOx	Burden Cost $/tonne clinker
SCR	Transferable	838	5.67	85%	712.3	0.85	$5,000	$12.00
LoTOX	Transferable	838	5.67	85%	712.3	0.85	$2,800	$6.80
SNCR	Innovative	838	5.67	35%	293.3	3.7	$2,100	$2.10
Wet to Dry	Available	1,802	5.67	65%	1,171.3	2.0	$6,700	$11.00
Large 3 Kiln SCR	Transferable	1,802	5.67	85%	1,531.7	0.85	$5,400	$8.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace exiting capacity.

TXI #2 and #3

TXI #2 began operation in 1963 and TXI #3 began operation in 1967. Similar to TXI #1 and #4, these are wet kilns that use the old process of making cement from wet slurry. Because the kilns are of similar size and used in a similar manner, one estimate has been created to represent both TXI #2 and TXI #3. Cost and control estimates are based on averaging the operation of these kilns. Although the kilns are physically similar to TXI #1 and #4, they are used as backup units. As backup units, these kilns have a low utilization rate (averaging 15% for the two kilns in 2004); the low utilization rate will show poor economics of control, as the fixed costs will be averaged over very small NO_x reductions. The control option for replacement of the wet kilns at TXI with a new large dry kiln of equal capacity to the old wet kilns is and option for all four kilns and has identical economics and environmental benefits as described above for TXI #1 and #4. Also, as with TXI #1 and #4, mid-kiln firing is assumed as the starting place for this analysis as this is already required the Texas regulations. The analyses for TXI #2 and #3 presented below are based on an average for the two kiln and values presented below, such as emissions reductions, should be doubled to account for both kilns.

Table 1-4 Summary of Technologies for TXI #2 & #3 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate $lbsNO_x$/tonne	Cost Effectiveness $/ton NO_x	Burden Cost $/tonne clinker
SCR	Transferable	85	3.4	85%	72.3	0.51	$60,000	$13.00
LoTOx	Transferable	85	3.4	85%	72.3	0.51	$8,000	$11.50
SNCR	Innovative	85	3.4	35%	30	2.2	$11,000	$6.50
Wet to Dry Large 3	Available	1,802	5.67	65%	1,171.3	2.0	$6,700	$11.00
Kiln SCR	Transferable	1,802	5.67	85%	1,531.7	0.85	$5,400	$8.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace exiting capacity.

TXI #5

TXI #5 began operation in 2001 and is the largest and most efficient kiln line in the study area. It is fuel efficient and intrinsically low in NO_x emissions. The low NO_x emissions rate is a function of the design and may also be partly the result of the chemistry of the feed materials (see discussion of chemistry in the main report) that may be causing reduction of NO_x. Because of the relatively low NO_x concentrations in the offgas, the expected NO_x removal efficiencies are lower for TXI #5 than for other kilns. For example, both European and US experience with SNCR indicates that removal is less efficient at lower NO_x concentration and that practical removal is currently understood to be limited to about 200 mg/m3 or 100 ppm. For this reason, TXI #5 is modeled for 35% control for SNCR compared to 50% for the Holcim kilns.

Table 1-5 Summary of Technologies for TXI #5 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control $lbsNO_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate $lbsNO_x$/tonne	Cost Effectiveness $/ton NO_x	Burden Cost $/tonne clinker
SCR	Available	1,710	1.50	80%	1,368	0.30	$1,300	$1.10
LoTOx	Transferable	1,710	1.50	80%	1,368	0.30	$2,400	$1.40
SNCR	Available	1,710	1.50	35%	598.5	1.0	$2,300	$0.60

1.1.3. Control Alternatives for Ash Grove Cement

ASH GROVE #1, #2 and #3

Ash Grove operates three wet kilns that began operation in 1966, 1969 and 1972. Similar to the wet kilns at TXI, these are wet kilns that use the older process of making cement from wet slurry. This makes high quality cement but uses substantially more energy to make cement. Both energy use and NO_x emissions rates are substantially higher for wet kilns that for dry process kilns. The Ash Grove kilns are currently complying with the SIP requirement for mid-kiln firing. The NO_x emissions rate at Ash Grove from mid-kiln firing of tires appears to be substantially lower than at TXI where the mid-kiln firing project has been delayed by permit issues.

Because the Ash Grove kilns are of similar size and used in a similar manner, separate discussions are not provided for each kiln. Slight differences in flow rates and emissions rates are modeled and presented in the tables below. Similar to the TXI presentation, a control option for replacement of the wet kilns at Ash Grove with a new large dry kiln of equal capacity to the old wet kilns is presented. A single, large SCR is modeled that combines the emissions and flow of the three kilns into one large control unit is modeled to demonstrate the impact on control costs. SCR is more cost effective at Ash Grove than at TXI due to higher gas temperatures and less required reheat of stack gas.

Table 1-6 Summary of Technologies for Ash Grove #1 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Transferable	702	5.57	85%	596.7	0.84	$5,200	$12.00
LoTOx	Transferable	702	5.57	85%	596.7	0.84	$2,900	$7.00
SNCR	Innovative	702	5.57	35%	245.7	3.6	$2,200	$2.20
Wet to Dry Large 3	Available	2,205	5.68	65%	1,433.3	2.0	$6,500	$11.00
Kiln SCR	Transferable	2,205	5.83	85%	1,874.25	0.88	$4,200	$10.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small.

Table 1-7 Summary of Technologies for Ash Grove #2 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNOx//tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbNOx/tonne	Cost Effectiveness $/ton NO_x	Burden Cost $/tonne clinker
SCR	Transferable	750	5.95	85%	637.5	0.89	$5,200	$13.00
LoTOx	Transferable	750	5.95	85%	637.5	0.89	$2,900	$7.50
SNCR	Innovative	750	5.95	35%	262.5	3.9	$2,200	$2.30
Wet to Dry Large 3	Available	2,205	5.68	65%	1,433.3	2.0	$6,500	$11.00
Kiln SCR	Transferable	2,205	5.83	85%	1,874.25	0.88	$4,200	$10.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small.

Table 1-8 Summary of Technologies for Ash Grove #3 – Full Year Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNOx/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNOx/tonne	Cost Effectiveness $/ton NO_x	Burden Cost $/tonne clinker
SCR	Transferable	764	6.06	85%	649.4	0.91	$5,500	$14.00
LoTOx	Transferable	764	6.06	85%	649.4	0.91	$3,000	$7.90
SNCR	Innovative	764	6.06	35%	267.4	3.9	$2,200	$2.30
Wet to Dry Large 3	Available	2,205	5.68	65%	1,433.3	2.0	$6,500	$11.00
Kiln SCR	Transferable	2,205	5.83	85%	1,874.3	0.88	$4,200	$10.00

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small.

1.1.4. Ozone Season Only Control Costs

The emissions reductions calculated in the tables below are based on operation of the control equipment during the Dallas/Ft. Worth ozone season unless otherwise noted. For example, SCR is presumed to operate only during the ozone season in the modeling. This results in a higher annualized cost effectiveness in dollars per ton of NO_x controlled as less NO_x is controlled on an annual basis. Wet kiln to dry preheat/precalciner unit conversions provide benefit for the full year and are not seasonal measures. Tables 1-9 through 1-16 are similar to Tables 1-1 through 1-8 except that adjustments have been made to represent seasonal operation.

Holcim Ozone Season Results

Table 1-9 Summary of Technologies for Holcim #1 – Ozone Season Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Available	2,222	3.76	85%	1,267.3	0.56	$1,950	$2.00
LoTOx	Transferable	2,222	3.76	85%	1,267.3	0.56	$2,400	$2.35
SNCR	Available	2,222	3.76	50%	745.4	1.9	$1,500	$1.00
Calciner Upgrade	Available	2,222	3.76	40%	888.8	2.2	$2,795	$2.70

Emissions reductions are for ozone season unless otherwise noted.
40% for new low-NOx calciner based on literature.
Cost effectiveness for calciner upgrade calculated by ratio of burden costs using SCR data.
Calciner upgrade is not a seasonal ozone measure.

Table 1-10 Summary of Technologies for Holcim #2 – Ozone Season Control

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Available	1,778	3.01	85%	1,014.0	0.45	$2,000	$1.70
LoTOx	Transferable	1,778	3.01	85%	1,014.0	0.45	$2,300	$1.90
SNCR	Available	1,778	3.01	50%	596.5	1.5	$1,700	$0.90

Emissions reductions are for ozone season unless otherwise noted.

TXI Ozone Season Results

Table 1-11 Summary of Technologies for TXI #1 & #4 – Ozone Season Only

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Transferable	838	5.67	85%	477.9	0.85	$5,500	$9.00
LoTOX	Transferable	838	5.67	85%	477.9	0.85	$3,300	$4.70
SNCR	Innovative	838	5.67	35%	196.8	3.7	$2,400	$1.60
Wet to Dry Large 3	Available	1,802	5.67	65%	1,171.3	2.0	$6,700	$11.00
Kiln SCR	Transferable	1,802	5.67	85%	1,027.7	0.85	$5,400	$6.00

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace exiting capacity, emissions reduction is full year.

Table 1-12 Summary of Technologies for TXI #2 & #3 – Ozone Season Only

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Transferable	85	3.4	85%	48	0.51	$90 000	$13.00
LoTOx	Transferable	85	3.4	85%	48	0.51	$11 000	$10.50
SNCR	Innovative	85	3.4	35%	20	2.2	$13 000	$5.00
Wet to Dry Large 3	Available	1,802	5.67	65%	1,171.3	2.0	$6,700	$11.00
Kiln SCR	Transferable	1,802	5.67	85%	1,027.7	0.85	$5,400	$6.00

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace exiting capacity, emissions reduction is full year.

Table 1-13 Summary of Technologies for TXI #5 – Ozone Season Only

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Available	1,710	1.50	80%	918.0	0.30	$2,200	$0.90
LoTOx	Transferable	1,710	1.50	80%	918.0	0.30	$2,600	$0.90
SNCR	Available	1,710	1.50	35%	401.6	1.0	$2,500	$0.45

Emissions reductions are for ozone season unless otherwise noted.

Ash Grove Ozone Season Results

Table 1-14 Summary of Technologies for Ash Grove #1 – Ozone Season Only

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Transferable	702	5.57	85%	400.4	0.84	$6 400	$9.10
LoTOx	Transferable	702	5.57	85%	400.4	0.84	$3 400	$5.00
SNCR	Innovative	702	5.57	35%	164.9	3.6	$2 500	$1.70
Wet to Dry Large 3	Available	2,205	5.68	65%	1,433.3	2.0	$6 500	$11.00
Kiln SCR	Transferable	2,205	5.83	85%	1,257.6	0.88	$5 100	$7.60

SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small, emissions reduction is full year.

Table 1-15 Summary of Technologies for Ash Grove #2 – Ozone Season Only

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Transferable	750	5.95	85%	427.8	0.89	$6,400	$9.80
LoTOx	Transferable	750	5.95	85%	427.8	0.89	$3,500	$5.40
SNCR	Innovative	750	5.95	35%	176.1	3.9	$2,400	$1.70
Wet to Dry Large 3	Available	2,205	5.68	65%	1,433.3	2.0	$6,500	$11.00
Kiln SCR	Transferable	2,205	5.83	85%	1,257.6	0.88	$5,100	$7.60

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small, emissions reduction is full year.

Table 1-16 Summary of Technologies for Ash Grove #3 – Ozone Season Only

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNO$_x$/tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbsNO$_x$/tonne	Cost Effectiveness $/ton NO$_x$	Burden Cost $/tonne clinker
SCR	Transferable	764	6.06	85%	435.7	0.91	$6,740	$10.50
LoTOx	Transferable	764	6.06	85%	435.7	0.91	$3,700	$5.70
SNCR	Innovative	764	6.06	35%	179.4	3.9	$2,400	$1.70
Wet to Dry Large 3	Available	2,205	5.68	65%	1,433.3	2.0	$6,500	$11.00
Kiln SCR	Transferable	2,205	5.83	85%	1,257.6	0.88	$5,100	$7.60

Emissions reductions are for ozone season unless otherwise noted.
SCR includes the cost of installing and operating RTO's to reheat gas after ESPs.
Wet to dry conversion analysis based on one large kiln to replace 3 small, emissions reduction is full year.

1.1.5. Summary of Performance and Cost Modeling Assumptions

The ERG Team used best engineering judgment in determining modeling parameters from the various data available. The ERG Team relied primarily on permit materials and emissions statements submitted to the State of Texas as well as material supplied by the companies in establishing the modeling parameters used to estimate control performance, cost and cost effectiveness. The ERG Team considered long term trends to derive estimated values for factors such as annual production capacity of clinker, which was adjusted by an assumed capacity factor that may be lower than current high operating levels. Values for airflows and temperatures were not always available for

the proposed control device locations and values were estimated based on temperature and moisture adjustments.

Cost effectiveness is calculated for NO_x reductions only. A wet to dry kiln conversion, calciner upgrade or the addition of a scrubber will result in reduction of other pollutants. As this study is performed to assess ozone control measures, these benefits have not been included in the cost benefit analyses. A simple spray tower that would not effectively control SO_2 is priced as part of the LoTOx analysis for wet kilns. If a flue gas desulfurization (FGD) scrubber were added, the price would increase. However, additional benefits for other pollutants controlled would also occur. Additional, voluntary control of other pollutants would bring emissions credits that could be sold. For example, adding FGD scrubbers to Ash Grove wet kilns could result in approximately 1,800 tons per year of SO_2 emissions reduction per kiln and a wet kiln conversion would result in approximately 1,300 tons per year of SO_2 reduction per kiln. Both the oxides of nitrogen and sulfur are also precursors of fine particle formation. Control technologies that remove these precursors would provide additional, unquantified benefits to regional air quality.

1.1.5.1. Kiln replacement or upgrading

Both kiln replacement and upgrading were considered for modeling for the wet kilns. Replacement is the only option actually modeled because none of the wet kilns are large enough to be practically upgraded to a semi-wet system. Semi-wet systems do result have been shown to result in significant production increases and NOx decreases but fuels savings have proven to be limited. Upgrading the preheater/calciner tower on Holcim #1 was also considered as an option. This process line is somewhat older than Holcim #2 or TXI #5 and is the design is somewhat less energy efficient. The cost values for wet to dry conversions and for upgrading the design of Holcim #1 as well as the energy improvements are taken primarily from Department of Energy reports.

1.1.5.2. SCR

The SCR cost model is a boiler cost model developed for use on coal-fired utility boilers. The SCR model is developed from the OAQPS Cost Manual and has been applied to other processes such as refinery FCCUs with reasonable success.

For the dry kilns, the model assumes that a location for SCR can be found where reheat of the process gas is not required. This is a high dust assumption. For the wet kilns, installation is assumed to be located after the dust collectors (low dust) and that reheat of the exhaust gas will be required. The reheat cost model is based on the OAQPS cost model for regenerative thermal oxidizers with 70% heat recovery.

Although current assumptions for coal-fired power plants would predict 90% or better control for SCR, this assumption has been lowered to 85% for these model runs. This was done to represent a conservative approach to the cost modeling that included consideration of potential problems in applying SCR such as higher variability of the gas stream comparing a utility boiler to a cement plant and lack of experience in achieving high levels of control using SCR in the cement industry. Due to the lower emissions rates at TXI #5, the control efficiency was modeled at 80%. This was based on the evaluation of the current relatively low concentrations of NO_x in the TXI stack and uncertainty about SCR performance in a cement kiln at very low endpoint concentrations. These control efficiencies are not intended to define the final performance of this technology, but to evaluate costs under conservative assumptions.

1.1.5.3. SNCR

The SNCR cost model is also a boiler cost model developed for use on coal-fired utility boilers. The SNCR model is derived from the OAQPS cost manual and EPA's OTAG cost modeling. It is has been simplified to obtain capital costs primarily on flow rates. The ERG team attempted to verify the reasonableness of this model's results for the Ellis County dry kilns. The estimates for wet kilns are conjecture. No accurate

costing can be developed without an understanding of the ultimate design of the control system. As SNCR experimentation as an innovative control options was deemed technically feasible, costs based on the dry kiln model were developed. Reagent costs are a substantial part of the annualized cost of SNCR, so this rough cost estimate for wet kilns was still considered to be a valuable approximation.

As with the SCR control efficiencies, the cost models were run at conservative control efficiency values. A value of 50% was used for the Holcim kilns and 35% was used for the TXI #5 and the wet kilns. The control efficiency of 35% at TXI was consistent with the reported performance of a European application at approximately 100 ppm. The value for wet kilns represented a reduced expectation for this experimental approach.

1.1.5.4. Oxidation Technologies

LoTOx

The LoTOx model is based on the OAQPS model for thermal oxidation. Specific inputs to this model were developed with assistance from BOC and should produce results reasonably close to the current costs of their oxidation technology. For the dry process kilns, no scrubbers were assumed to be required as the existing scrubbers were expected to be sufficient for removal of oxidation products from the process gas. For the wet kilns, BOC provided approximate costs for installing LoTOx with spray towers. BOC provided generalized costs and detailed costs on scrubber operating costs have not been developed.

The same control efficiencies were used for LoTOx as for SCR. Again, this was done to make the cost estimates conservative due to lack of application of these technologies to the cement industry. BOC asserted that controls efficiencies of 95% and 98% could be obtained using this technology. However, for this modeling effort, the same performance levels were modeled for LoTOx as for SCR. As with the SCR modeling, this was not done as a reflection on the final performance capability of the

technology, but rather to provide an equivalent and conservative basis for evaluating the cost of control.

The accuracy of OAQPS cost modeling approaches is typically within 30% or so for instances where parameters are accurately defined and the process well known. This is a useful tool for comparing different technologies. However, closely scrutinized vendor quotes should be the basis of any final comparison of technologies. Minor differences in modeling results are likely to be the product of assumptions regarding cost of electricity or reagents. For example, for Holcim #2, the cost of SCR was predicted to be $1,700 per ton of NO_x and LoTOx was modeled at $2,100 per cost. As discussed above, we may have slightly underestimated the control efficiency of SCR and LoTOx.

A relatively small difference in the cost effectiveness for SCR and LoTOx should not be viewed as significant without understanding the contributing factors. Reagent cost and control efficiency assumptions can account for these differences. Reagent cost for ammonia is currently very volatile due to high natural gas costs. A value of $500 per ton was used to reflect higher costs experienced in 2005, but not the currently higher short-term prices. If current high prices persist, the cost difference between these two technologies would be negligible. If LoTOx proves better at responding to fluctuations in NO_x concentrations and achieves a higher level of control than SCR, this would also tend to push cost effectiveness of the two technologies closer together. Differences of 20% in the cost effectiveness of two technologies should not a basis for selecting one technology over another. If initial modeling results produce similar economic and performance values, both technologies should be considered for vendor pricing unless other factors dictate a clear preference for one over the other. Other factors, such as a determination that reheat was needed for application of SCR to dry kilns would have a substantial impact and the two technologies would no longer appear equivalent in cost effectiveness.

Other Oxidation Technologies

There are other oxidation technologies using hydrogen peroxide or other chemical reagents. Most of these technologies are new; relatively low temperature end-of-pipe control techniques. As mentioned under the discussion for SCR above, the reagent cost

for ammonia reagents is currently high. Other oxidation technologies may allow use of lower cost reagents that may improve cost effectiveness for plants with existing wet scrubbers. There is one higher temperature hydrogen peroxide technology that may be able to be implemented inside an existing precalciner system, although it still requires a wet scrubber. At current hydrogen peroxide commodity prices, one of these alternative technologies may be more cost effective than ozone or ammonia based reagent alternatives. None of these technologies were found to have been used on a cement kiln or comparable system. Therefore, costing of these options was not attempted. All of these systems should be considered innovative but should not be ruled out of consideration as a lower cost reagent would have a substantial impact on annual control costs.

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ASSESSMENT OF NO$_x$ EMISSIONS REDUCTION STRATEGIES FOR CEMENT KILNS - ELLIS COUNTY

DRAFT FINAL REPORT

TCEQ Contract No. 582-04-65589
Work Order No.05-06

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This study is the work project of a panel of experts assembled at the request of the Texas Commission on Environmental Quality. This study was performed under contract to Eastern Research Group that provided overall contract management and subcontracted the outside experts and laboratory services. While each of the experts brought specific skills to this study and was the principal author of individual sections of the report, the overall study represents a team effort. The general conclusions of the study have been reviewed and are endorsed by the entire expert panel.

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2.0. DEFINING PARAMETERS FOR CONTROL EVALUATION

This section of the report is taken from the EPA 2000 Report and is included, with minor editing by the ERG Team. This information is included to provide the Texas environmental communities with the comprehensive background information necessary to understand the parameters that dictate NO_x control options at cement kilns.

2.1. Overview of Portland Cement Manufacturing Process and NO_x Generation

Portland cement, a fine gray or white powder, is the generic term for the type of cement used in virtually all concrete, which is a mixture of aggregates (e.g., crushed stone, gravel, sand), water, and cement. The American Society for Testing and Materials (ASTM) defines portland cement as "hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter ground addition."

In 2004, the portland cement industry in the U.S. consisted of 114 facilities in 37 States (and 2 facilities in Puerto Rico). Approximately 90 million tons of portland cement were produced in 2004, with California, Texas, Pennsylvania, Michigan, Missouri, and Alabama accounting for approximately 50 percent of the production [USGS].

Hydraulic portland cement, the primary product of the cement industry, is made from clinker blended with gypsum. Clinker is produced by heating a mixture of limestone, clay, and other ingredients to incipient fusion at a high temperature. Limestone is the single largest ingredient required in the cement-making process, and most cement plants are located near large limestone deposits. Portland cement is used in almost all construction applications including homes, public buildings, roads, industrial plants, dams, bridges, and many other structures.

In the cement-making process, the solid raw materials are heated to their fusion temperature, typically 1400 to 1500 EC (2550 to 2750 EF), by burning various fuels such as coal. Portland cement has been defined as "a hydraulic cement produced by pulverizing portland cement clinker and usually containing calcium sulfate."[1] Portland-cement clinker has been defined as "a clinker, partially fused by pyroprocessing, consisting predominantly of crystalline hydraulic calcium silicates."[1] Burning an appropriately proportioned mixture of raw materials at

a suitable temperature produces hard fused nodules called clinker, which are further ground to a desired fineness.

Five types of portland cement are recognized in the United States which contain varying amounts of the basic clinker compounds given in Table 3-1.[2] Different types of cements are produced by starting with appropriate kiln feed composition, blending the clinker with the desired amount of calcium sulfate, and grinding the product mixture to appropriate fineness. Manufacture of cements of all of the various types involves the same basic high temperature fusion and clinkering process responsible for the NO_x emissions from cement kilns.

The five basic types of portland cement recognized and produced in the United States are described below.[2,3] In addition, different varieties are prepared by using various blending formulations.[4]

Type I portland cement is a normal, general-purpose cement suitable for all uses. It is used in general construction projects such as buildings, bridges, floors, pavements, and other precast concrete products. Type I is also known as regular cement and most commonly known as gray cement because of its color. White cement typically contains less ferric oxide and is used for special applications. There are other types of cements in general use such as oil-well cement, quick-setting cement, and others for special applications. Type IA portland cement is similar to Type I with the addition of air-entraining properties.

Table 2-1. Basic Clinker Compounds[2]Formula	Name
$2CaO@SiO_2$	Dicalcium silicate
$3CaO@SiO_2$	Tricalcium silicate
$3CaO@AL_2O_3$	Tricalcium aluminate
$4CaO@Al_2O_3@Fe_2O_3$	Tetracalcium aluminoferrite
MgO	Magnesium oxide in free state or combined in di- or tri-calcium silicate lattice.

Type II portland cement generates less heat at a slower rate and has a moderate resistance to sulfate attack. Type II portland cements are for use where moderate heat of hydration is required or for general concrete construction exposed to moderate sulfate action. Type IIA portland cement is identical to Type II, with the exception of inclusion of an air-entraining admixture, and produces air-entrained concrete.

Type III portland cement is a high-early-strength cement and causes concrete to set and gain strength rapidly. Type III is chemically and physically similar to Type I, except that its particles have been ground finer. It is made from raw materials with a lime to silica ratio higher than that of Type I cement. They contain a higher proportion of tricalcium silicate ($3CaO \cdot SiO_2$) than regular portland cements. Type IIIA is an air-entraining, high-early-strength cement.

Type IV portland cement has a low heat of hydration and develops strength at a slower rate than other cement types, making it ideal for use in dams and other massive concrete structures where there is little chance for heat to escape. Type IV portland cement contains a lower percentage of tricalcium silicate ($3CaO \cdot SiO_2$) and tricalcium aluminate ($3CaO \cdot Al_2O_3$) than type I, thus lowering the heat evolution. Consequently, the percentage of dicalcium silicate is increased substantially and the percentage of tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) may be increased or may stay the same.

Type V portland cement is used only in concrete structure that will be exposed to severe sulfate action, principally where concrete is exposed to soil and groundwater with a high sulfate content. Type V portland cement are those which, by their composition or processing, resist sulfates better than the other four types.

The use of air-entraining agents increases the resistance of the hardened concrete to scaling from alternate freezing and thawing. By adding these materials to the first three types of cements, IA, IIA, and IIIA varieties of cements are produced. Additional varieties of cements are produced for special applications by blending different ingredients: masonry cement, expansive cement, oil-well cement, etc. Masonry cements are commonly finely ground mixtures of portland cement, limestone, and air-entraining agents. Granulated blast furnace slags and natural or artificial pozzolans are mixed and interground with portland cement to prepare still other varieties such as blended types IP, IS, S, I(PM), and I(SM).[4]

2.1.1. Description of the Cement Industry

About 77.6 million metric tons of gray portland and 274,000 metric tons of white cement were produced in a total of 198 cement kilns at 118 plants in the United States in 1998.[5] This was a 6.0 percent increase from the 1990 reported total production of 73.5 million metric tons. As shown in Figure 3-1, cement industry annual clinker capacity steadily declined from the 1975 peak through 1990 and has steadily increased since the 1990 low. While the number of kilns has dropped off sharply, average kiln size has increased. Since 1973 when average kiln size was 173,000 metric tons, average kiln size has now reached 393,000 metric tons. Although 42 cement companies produced clinker in 1998, the top 5 companies provided about 44.2 percent of the total finish grinding capacity. This is evidence of a high concentration of the U.S. production among a limited number of top producers. Table 2-2 provides a list of all companies along with their share of the total clinker production. Table 2-3 lists the clinker producing capacity in the United States by States. The locations of the operating kilns are shown in Figure 2-2. California and Texas are the two largest states in terms of clinker capacity with Pennsylvania, Missouri, and Alabama rounding out the top five. Fourteen states and the District of Columbia had no cement clinker-producing plants in 1998.[5]

The large majority of the cement plants (about 82.4 percent) in the United States are coal fired with about 2.8 percent using natural gas, and 0.9 percent using oil as the primary fuel.[5] The remaining 13.9 percent of the plants used other combinations, e.g. coal/waste as primary fuel. In 1998, 11 plants used waste as a primary fuel with 49 plants reporting waste as an alternate fuel.

The process of portland cement manufacture consists of:[6]

- Quarrying and crushing the rock,
- Grinding the carefully proportioned materials to high fineness,
- Subjecting the raw mix to pyroprocessing in a rotary kiln, and
- Grinding the resulting clinker to a fine powder.

A layout of a typical plant is shown in Figure 3-3, which also illustrates differences between the two primary types of cement processes: wet process and dry process.[6] Newer designs of dry process plants are equipped with innovations such as precalciners and/or suspension preheaters to increase the overall energy efficiency of the cement plant.[6] Figure 3-4 is an illustration of a preheater/precalciner type of dry process system.[7]

The choice between the wet or dry process for cement manufacturing often depends upon the moisture content in the raw feed materials mined from quarries. If the moisture content of the feed materials is already very high (15 to 20 percent), a wet process may be attractive. The recent trend, however, has been toward the dry process with preheater/precalciner systems. In 1998, about 20.6 million metric tons of clinker were produced by the wet process with 57.4 million metric tons produced by a dry process. Within the dry process category, 14.2 million metric tons were produced by facilities equipped with a preheater system and 26.1 million metric tons were produced by facilities equipped with a precalciner system.[5]

The different steps involved in the cement manufacturing process are described in the following subsections.

Raw Materials and Kiln Feed Preparation

Calcium carbonate and the oxides of silicon, aluminum, and iron comprise the basic ingredients of cement raw mix. Because of the large requirement for calcium, the plants are generally located near the source of the calcareous material. The requisite silica and alumina may be derived from a clay, shale, or overburden from a limestone quarry. Such materials usually contain some of the required iron oxide, but many plants need to supplement the iron with mill scale, pyrite cinders, or iron ore. Silica may be supplemented by adding sand to the raw mix, whereas alumina can be furnished by bauxites and alumina-rich flint clays.[6] Industrial

byproducts are becoming more widely used as raw materials for cement, e.g., slags contain carbonate-free lime, as well as substantial levels of silica and alumina. Fly ash from utility boilers can often be a suitable feed component, since it is already finely divided and provides silica and alumina.

The bulk of raw materials originates in the plant quarry. A primary jaw or roll crusher is frequently located within the quarry and reduces the quarried limestone or shale to about 100 mm top size. A secondary crusher, usually roll or hammer mills, typically gives a product of about 10 to 25 mm top size. Combination crusher-dryers can utilize exit gases from the kiln or clinker cooler to dry wet material during crushing. Each of the raw materials is stored separately and proportioned into the grinding mills separately using weigh feeders or volumetric measurements. Ball mills are used for both wet and dry processes to grind the material to a fineness such that only 15 to 30 wt% is retained on a 74-μm (200 mesh) sieve.

In the wet process the raw materials are ground with about 30 to 40 percent water, producing a well-homogenized mixture called slurry. Raw material for dry process plants is ground in closed-circuit ball mills with air separators, which may be adjusted for the desired fineness. Drying may be carried out in separate units, but most often is accomplished in the raw mill simultaneously with grinding. Waste heat can be utilized directly in the mill by coupling the raw mill to the kiln- and/or clinker cooler exhaust. For suspension preheater-type kilns, a roller mill utilizes the exit gas from the preheater to dry the material in suspension in the mill. A blending system provides the kiln with a homogeneous raw feed. In the wet process the mill slurry is blended in a series of continuously agitated tanks in which the composition, usually the calcium oxide content, is adjusted as required. These tanks may also serve as kiln feed tanks or the slurry may be pumped to large kiln feed basins. Dry process blending is usually accomplished in a silo with compressed air.[6]

Pyroprocessing

All cement clinker is produced in large rotary kiln systems. The rotary kiln is a refractory brick-lined cylindrical steel shell [3 to 8 m (10 to 25 ft) diameter, 50 to 230 m (150 to 750 ft) long] equipped with an electrical drive to rotate the kiln on its longitudinal axis at 1 to 3 rpm. It is a countercurrent heating device slightly inclined to the horizontal, so that material fed into the upper end travels slowly by gravity to be discharged into the clinker cooler at the lower,

discharge end. The burners at the firing end, i.e., the lower or discharge end, produce a current of hot gases that heats the clinker, and the calcined and raw materials in succession, as it passes upward toward the feed end. Refractory bricks of magnesia, alumina, or chrome-magnesite combinations line the firing end. In the less heat-intensive midsection of the kiln, bricks of lower thermal conductivity are often used. Abrasion-resistant bricks or monolithic castable linings are used at the feed end.[6]

Pyroprocessing may be conveniently divided into four stages, as a function of location and temperature of the materials in the rotary kiln.[8]

1. Evaporation of uncombined water from raw materials, as material temperature increases to 100°C (212°F);
2. Dehydration, as the material temperature increases from 100°C to approximately 430°C (800°F) to form dehydrated clay minerals composed of oxides of silicon, aluminum, and iron;
3. Calcination, during which carbon dioxide (CO_2) and CaO are formed from calcium carbonates, primarily between 900°C (1,650°F) and 982°C (1,800 °F); and
4. Reaction, of the oxides in the burning zone of the rotary kiln, to form cement clinker at temperatures of approximately 1,510°C (2,750°F).

The duration and location of these stages in an actual kiln depend upon the type of process used, e.g., wet or dry, and the use of preheaters and precalciners as discussed in the following section.

It is desirable to cool the clinker rapidly as it leaves the burning zone. Heat recovery, preheating of combustion air, and fast clinker cooling are achieved by clinker coolers of the reciprocating-grate, planetary, rotary, or shaft type. Most commonly used are grate coolers where the clinker is conveyed along the grate and subjected to cooling by ambient air, which passes through the clinker bed in cross-current heat exchange. The air is moved by a series of undergrate fans and becomes preheated to 370 to 1,000°C (700 to 1,830°F) at the hot end of cooler. A portion of the heated air serves as secondary combustion air in the kiln. Primary air is that portion of the combustion air needed to carry the fuel into the kiln and disperse the fuel.[6]

2.1.2. Kiln Types and Operation

There are four main types of kilns used in portland cement manufacture:

- long wet kilns,

- long dry kilns,
- dry kilns with preheaters, and
- dry kilns with precalciners.

Wet kilns tend to be older units and are often located where the moisture content of feed materials from local sources (quarries) tends to be high. [MRPO]

Long Wet Kilns

In a long wet-process kiln, the slurry introduced into the feed end first undergoes simultaneous heating and drying. The refractory lining is alternately heated by the gases when exposed and cooled by the slurry when immersed; thus, the lining serves to transfer heat as do the gases themselves. Large quantities of water must be evaporated; thus most wet kilns are equipped with chains suspended across the cross section of the kiln to maximize heat transfer from the gases to the slurry, or chain garlands that serve to recuperate heat and simultaneously convey the slurry. After most of the moisture has been evaporated, the nodules, which still contain combined water, move down the kiln and are gradually heated to about 550°C (1,022°F) where the calcination reactions commence. The calcined material further undergoes clinkering reactions. As the charge leaves the burning zone and begins to cool, clinker minerals crystallize from the melt, and the liquid phase solidifies. The granular clinker material drops into the clinker cooler for further cooling by air.[6]

Wet kilns typically represent an older cement technology with smaller capacity kilns. In the United States wet cement kiln capacities range from 77,000 to 1,179,000 metric tons/year with an average of 307,000 metric tons/year.[5]

Dry Process Kilns

The dry process utilizes a dry kiln feed rather than a slurry. Early dry process kilns were short, and the substantial quantities of waste heat in the exit gases from such kilns were frequently used in boilers to generate electric power which often satisfied all electrical needs of the plant. In one modification, the kiln has been lengthened to nearly the length of wet-process kilns and chains were added. The chains serve almost exclusively a heat exchange function. Refractory heat-recuperative devices, such as crosses, lifters, and trefoils, have also been

installed. So equipped, the long dry kiln is capable of better energy efficiency than wet kilns. Other than the need for evaporation of water, its operation is similar to that of a wet kiln. To improve the energy efficiency of the dry process, variations such as suspension preheaters and precalciners have been introduced as discussed in the next sections.[6]

Long dry process kilns are generally of a smaller capacity compared to long wet kilns. In the United States dry cement kiln capacities range from 50,000 to 590,000 metric tons/year with an average capacity of 265,000 metric tons/year.[5]

Dry Kilns With Preheaters

In dry kilns with suspension preheaters, the pulverized feed passes by gravity through a series of cyclones and riser ducts in a vertical arrangement, where it is separated and preheated several times, typically in a four-stage cyclone system. The partially (40 to 50 percent) calcined feed exits the preheater tower into the kiln at about 800 to 900°C (1,500 to 1,650 °F). The kiln length required for completion of the cement formation is considerably shorter than that of conventional kilns, and heat exchange is very good. Suspension preheater kilns are very energy efficient compared to wet or long dry kilns. The intimate mixing of the hot gases and feed in the preheater riser ducts promotes condensation of alkalies and sulfur on the feed, which sometimes results in objectionable high alkali and sulfur contents in the clinker, or occasions buildups in the preheater tower. . To alleviate this problem, some of the kiln exit gases can bypass the preheater through a slip stream, or fewer cyclone stages can be used in the preheater with some sacrifice of efficiency.

Suspension preheater kilns represent a newer cement technology compared to the long dry kilns. They are also somewhat larger in production capacity than the conventional long rotary kilns. In the United States the preheater type kiln capacities range from 223,000 to 1,237,000 metric tons/year with an average capacity of 406,000 metric tons/year.

Dry Kilns With Precalciners

The success of preheater kiln systems, led to precalciner kiln systems. These units utilize a second burner to carry out calcination in a separate vessel attached to the preheater. The

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calciner utilizes preheated combustion air drawn from the clinker cooler or kiln exit gases and is equipped with a burner that typically burns about 60 percent of the total kiln fuel. Most often coal is used as a fuel in a calciner furnace; however, almost any fuel may be used including chipped tires. The raw material is calcined almost 95 percent, and the gases continue their upward movement through successive cyclone/riser duct preheater stages in the same manner as in an ordinary preheater. The precalciner system permits the use of smaller dimension kilns, since only actual clinkering is carried out in the rotary kiln. Energy efficiency is often even better than that of a preheater kiln, and the energy penalty for bypass of kiln exit gases is reduced since only about 40 percent of the fuel is being burned in the kiln. The burning process and the clinker cooling operations for the modern dry-process kilns are the same as for long wet kilns.

The precalciner technology is the most modern cement manufacturing technology and almost all of the newer cement plants are based on these designs. Precalciner kilns are also much larger in capacity than the conventional rotary kilns. The precalciner type kilns in the United States range from 449,000 to 1,580,000 metric tons/year with an average of 869,000 metric tons/year. Because of the new large precalciner plants replacing older and smaller plants, the overall average kiln capacity has been steadily increasing in the United States. It has increased from an average of 239,000 metric tons/year in 1980 to an average capacity of 393,000 metric tons/year in 1989.

Finish Grinding

The cooled clinker is conveyed to clinker storage. It is subsequently mixed with 4 to 6 percent gypsum and introduced directly into the finish mills. These are large, steel cylinders [2 to 5 m (7 to 16 ft) in diameter] containing a charge of steel balls, that rotate at about 15 to 20 rpm. Rarely, the desired size reduction may be accomplished in a roller mill, rather than in ball mills. Recently, the industry has also adopted the use of roller presses to precrush the clinker to smaller size prior to introduction to the finish mills. The roller press is more efficient than the crushing stage of the ball mill, and production capacities of finish grinding systems have been substantially increased and electrical energy requirements reduced by the incorporation of roller presses into finish circuits. The clinker and gypsum are ultimately ground to a fine, homogeneous powder. About 85 to 96 percent of the product is in particles less than 44 μm in diameter. This grinding may be accomplished by two different mill systems. In open-circuit

milling, the material passes directly through the mill without any separation. A wide particle size distribution range is usually obtained with substantial amounts of very fine and rather coarse particles. Open circuit grinding is, however, rarely practiced in U.S. cement plants. In closed-circuit grinding, the mill product is carried to a cyclonic air separator in which the coarse particles are rejected from the product and returned to the mill for further grinding.[6]

Quality Control

Beginning at the quarry operation, quality of the end product is maintained by adjustments of composition, burning conditions, and finish grinding. Control checks are made for fineness of materials, chemical composition, and uniformity. Clinker burning is often monitored by the liter weight test (which involves weighing a portion of sized clinker), a free lime test, or may be checked by microscopic evaluation of the crystalline structure of the clinker compounds. Samples may be analyzed by wet chemistry, X-ray fluorescence, atomic absorption, or flame photometry. Standard cement samples are available from the National Institute of Standards and Technology. Fineness of the cement is most commonly measured by the air permeability method. Finally, standardized performance tests are conducted on the finished cement.[6]

2.1.3. Thermal Characteristics

Figure 2-1 Provide a detailed look at the material and gas temperatures inside cement kilns. The concepts of high-grade heat and low-grade heat are well discussed by Weber.1 Weber states, "The boundary between the main and the subsidiary thermal system is assumed always to correspond to a material temperature of 550°C, since decarbonation in the rotary kiln in general already begins at this temperature. A certain amount of heat whose temperature is below the gas temperature at the commencement of decarbonation will always be left over from the calcining zone. This heat is "lower-grade" in the sense that, because of the low temperature, it cannot be further used for decarbonation or sintering, but only for preheating and drying."

In turn, Figure 2-2 provide a graphical look at the relationship between temperatures in the cement manufacturing process and the chemistry of cement clinker formation. Except for the process of drying the raw material slurry in wet kilns these profiles are essentially the same for

both wet and dry process cement kilns. The only substantive difference is that the difference between the gas and material temperature in a preheater tower is less than in the back end of a wet kiln because of the more efficient heat transfer in the cyclones.

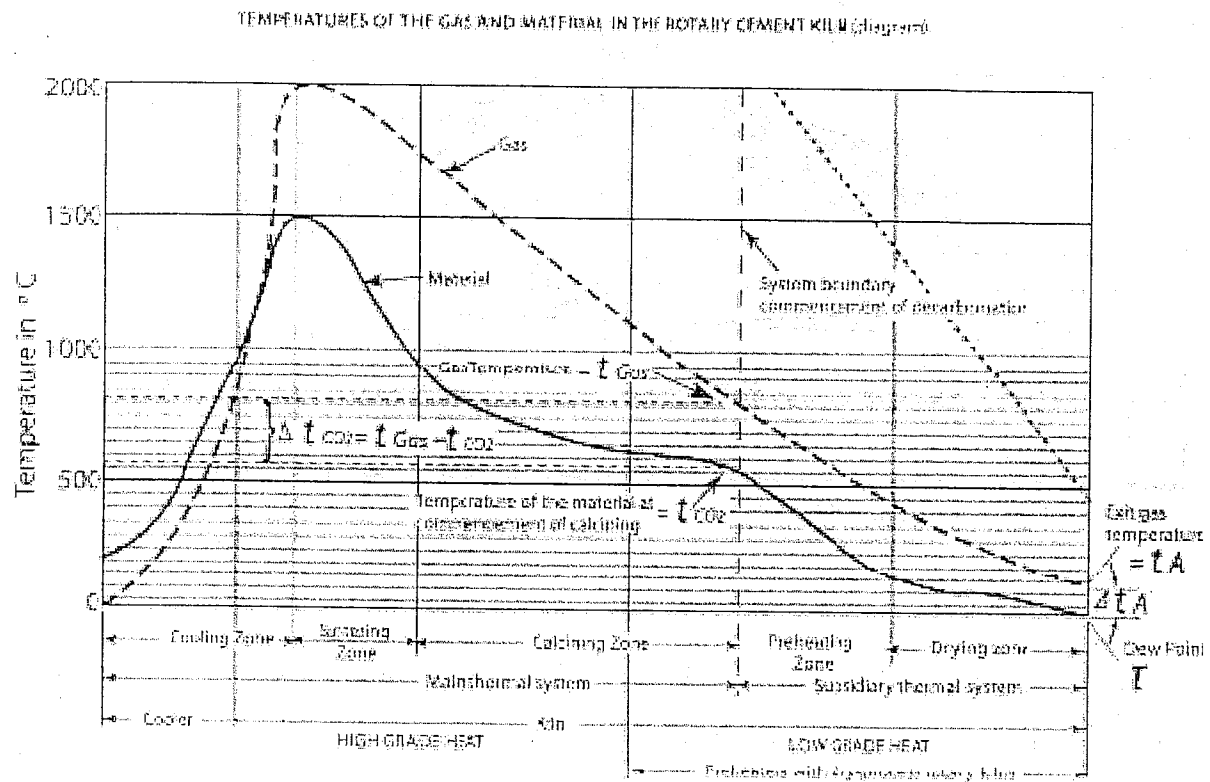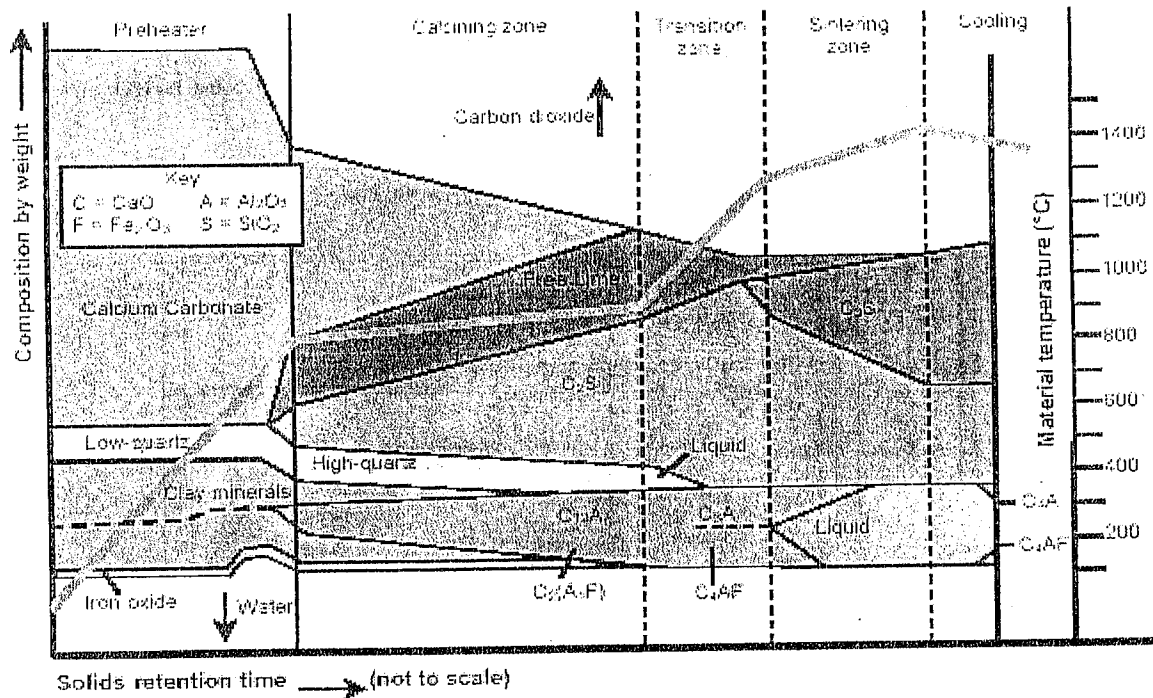**Figure 2-1 Temperature of the Gas and Material in the Rotary Cement Kiln1**

TEMPERATURES OF THE GAS AND MATERIAL IN THE ROTARY CEMENT KILN (diagram)

Figure 2-2 The Relationship Between Process Temperatures and the Chemistry of Cement Clinker Formation

References

1. Weber, Dr. Paul, Heat Transfer in Rotary Kiln with due Regard to Cyclic Processes and Phase Formation, Bauverlag GmbH Wiesbaden, 1963

2.1.4. Process Variables

The formation of clinker of suitable quality for manufacture of portland cement depends on the characteristics of feed materials and the temperature profile of the pyroprocessing step. The most critical process variables are:

- feed composition,
- feed particlesize,
- feed moisture concentration,
- feed mass flow rate,
- system heat losses, and
- ambient air infiltration.

More than 30 raw materials (primarily calcium carbonate, aluminosilicates, silica and iron oxide) are known to be used in portland cement manufacturing. [AP-42] These materials are ground and mixed to create a feed that has the appropriate chemical and physical properties to produce clinker with the desired properties. Uniform feed composition and size ensure consistent quality and characteristics of the clinker produced.

Higher moisture contents require more heat input to maintain proper temperature profile in the kiln. Cement raw materials are received with an initial moisture content varying from 1 to more than 50 percent. In dry kilns, the moisture content is usually reduced to less than 1 percent before or during the grinding process (e.g., using drum dryers, air separators, or supplying supplemental heat to the raw mill). In the wet process, water is added to the raw mill during the grinding of the raw materials, thereby producing a slurry of approximately 65 percent solids. [AP-42]

3.0 NO$_x$ FORMATION IN CEMENT KILNS

This section of the report is taken from the EPA 2000 Report and is included, with minor editing by the ERG Team. This information is included to provide the Texas environmental communities with the comprehensive background information necessary to understand the parameters that dictate NO$_x$ control options at cement kilns.
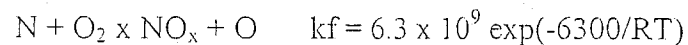
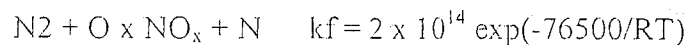## 3.1. Overview of NO$_x$ Formation Mechanisms

In cement manufacturing, conditions favorable for formation of nitrogen oxides (NO$_x$) are reached routinely because of the high process temperatures involved. Essentially, all of the NO$_x$ emissions associated with cement manufacturing are generated in the cement kilns. Although, there are other heating operations in a cement plant, such as drying of raw feed or coal, often the heat from the kiln exhaust gases is used for these operations making their contribution to NO$_x$ emissions negligible. In cement kilns, NO$_x$ emissions are formed during fuel combustion by two primary mechanisms:

- • Oxidation of the molecular nitrogen present in the combustion air which is termed thermal NO$_x$ formation, and

- • Oxidation of the nitrogen compounds present in the fuel which is termed fuel NO$_x$ formation.

Sometimes the raw material feed to the kiln may also contain nitrogen compounds which may lead to feed NO$_x$ formation similar to fuel NO$_x$ formation. Because of the high temperatures involved in the burning or clinker formation step, the thermal NO$_x$ formation provides the dominant mechanism for NO$_x$ formation in cement manufacturing. The term NO$_x$ includes both NO and NO$_2$ species, although NO$_2$ normally accounts for less than 10 percent of the NO$_x$ emissions from a cement kiln exhaust stack.[1] The concentration and emission of NO$_x$ are, however, typically expressed in equivalent NO$_2$ form.

3.1.1. Thermal NO$_x$ Formation

Thermal NO$_x$ is formed by the homogeneous reaction of oxygen and nitrogen in the gas phase at high temperatures. In the overall reaction mechanism proposed by Zeldovich,[2] the two important steps in NO$_x$ formation are given as:

$$N2 + O \times NO_x + N \quad kf = 2 \times 10^{14} \exp(-76500/RT)$$

$$N + O_2 \times NO_x + O \quad kf = 6.3 \times 10^9 \exp(-6300/RT)$$

where kf are the rate constants for the reactions shown. The high activation energy of reaction (4-1), 76.5 kcal/mol, means that this reaction is the most temperature sensitive. An equilibrium reaction of NO$_x$ with O$_2$ further results in NO$_2$ formation.

The equilibrium concentrations of NO$_x$ and NO$_2$ formed thus depend strongly upon the gas-phase temperature as well as the concentration of O$_2$ and N$_2$ in the gas phase. Table 3-1 shows the equilibrium concentrations of NO and NO$_2$ for two conditions.[3] First, the equilibrium concentrations of NO$_x$ and NO$_2$ for N$_2$ and O$_2$ concentrations found in ambient air are shown Secondly, Table 3-1 also shows the NO$_x$ and NO$_2$ concentrations at flue gas conditions where the O$_2$ and N$_2$ concentrations are defined for this table as 3.3 percent O$_2$ and 76 percent N$_2$. The equilibrium NO$_x$ concentrations for the flue gas conditions are lower than those for ambient conditions due to the lower O$_2$ concentration. The excess air used during fuel combustion can substantially affect NO$_x$ formation by determining the amount of oxygen available for NO$_x$ reaction. The cement kiln burning zones usually have about 5 to 10 percent excess air while higher excess air levels are not uncommon. Figure 3-1 shows the theoretical equilibrium concentrations of NO in the flue gas for different excess air levels.[1] As can be seen from this figure, over 1000 ppm of NO may possibly be formed at the typical kiln solids temperatures of 1430 to 1480°C (2600 to 2700°F) as the corresponding gas-phase temperatures are on the order of 1650°C (3000°F).

**Table 3-1. Calculated Equilibrium Concentrations (In PPM)
Of NOx and NOx In Air and Flue Gas [3]**

Temperature		Air		Flue Gas	
K	°F	NO	NO2	NO	NO2
300	80	$3.4(10)^{-10}$	$2.1(10)^{-4}$	$1.1(10)^{-10}$	$3.310)^{-3}$
800	980	2.3	0.7	0.8	0.1
1440	2060	800	5.6	250	0.9

Fuel combustion in the kiln burning zone is the primary source of thermal NO_x, formation in cement kilns due to temperatures well above 1,400°C (2,550°F). In contrast, the fuel combustion temperature in a precalciner or in a kiln riser duct is well below 1,200°C (2,200°F), suppressing thermal NO_x formation.[4] Mainly fuel and feed NO_x may be formed in the secondary firing zone of preheater and precalciner kiln systems. Along with the combustion temperature, the gas-phase residence time and the available oxygen concentration in the high temperature kiln burning zone are important parameters. Longer residence times at the high temperatures will allow the NO to be formed in the equilibrium quantities. Greater amounts of oxygen in the combustion zone will of course lead to greater amounts of NO formation. Once formed, the decomposition of NO at lower temperatures, although thermodynamically favorable, is kinetically limited. Thus, strategies to reduce NO_x emissions need to be based upon reducing formation of NO_x which may be achieved by reducing combustion temperature, oxygen concentration in the high temperature combustion zone, and the gas residence time at high temperatures.

3.1.2. Fuel NOx Formation

Fuel NO_x is formed by the conversion of nitrogen present in the fuel used. A recent survey of the cement industry by Portland Cement Association (PCA) indicates that almost 82 percent of the energy requirement of the cement industry is provided by coal.[5] Natural gas contributed about 3 percent of the energy demand, oil about 1 percent, and other fuels such as waste solvents provided about 14 percent of the energy. Both oil and natural gas have relatively low fuelbound nitrogen content, whereas coal may contain 1 to 3 percent of nitrogen by weight depending upon the source of coal. Waste-derived fuels (WDF) such as scrap tires, used motor

oils. surplus printing inks, dry-cleaning solvents, paint thinners, sludge from the petroleum industry, agricultural wastes such as almond shells, and even municipal biosolids (dewatered sewage sludge) are finding an increasing application in the cement kilns.[6] The nitrogen content in these fuels may be significant depending on the chemicals included in the waste mix being burned.

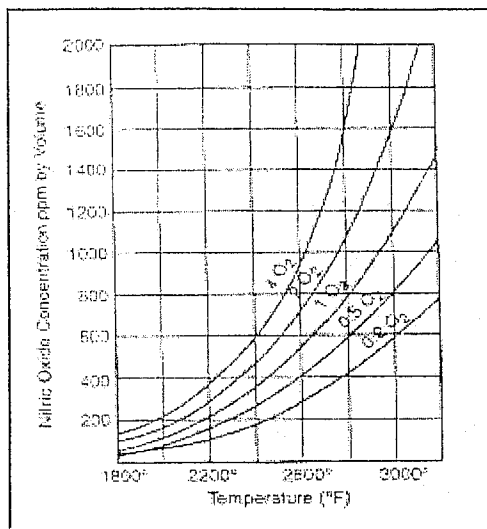**Figure 3.1. Theoretical equilibrium concentrations of NOx**

Figure 4-1. Theoretical equilibrium concentrations of NO in gas from combustion sustained in air.[1]

The maximum possible fuel NO_x formation may be estimated from the fuel nitrogen content by assuming 100 percent nitrogen conversion. The typical heat requirement for a wet process is estimated to be about 6 million Btu for a ton of clinker and the corresponding requirement for a dry process is estimated to be about 4.5 million Btu for a ton of clinker. Assuming an average heat requirement of 5.3 million Btu for a ton of clinker, and a coal heating value of 12,000 Btu/lb, about 442 lb of coal will be required per ton of clinker produced. With a nitrogen content of 1 percent by weight, approximately 9.5 lb of NO (14.5 lb expressed as NO_2) would be produced per ton of clinker with 100 percent nitrogen conversion. Thus, even with only 10 percent conversion of coal nitrogen to NO_x, 1.5 lb of fuel NO_x (expressed as NO_2) may be formed per ton of clinker when coal is used as a primary fuel.

The amount of fuel NO_x formed is difficult to identify separately from thermal NO_x as measurements indicate the overall NO_x formed. In general, however, thermal NO_x is assumed to

be the dominant mechanism in cement kilns.[7] Typically, gas burners produce more intense and hot flames compared to the less intense "lazy" flames produced by coal burners. Thus, gas-fired kilns may be expected to produce greater thermal NO_x as compared to coal-fired kilns. Coal, on the other hand, contains much greater amounts of fuel-bound nitrogen than natural gas which has almost no fuel-bound nitrogen. The coal-fired kilns may thus be expected to produce more fuel NO_x than gas-fired kilns. A study of gas- and coal-fired kilns, however, clearly indicated that gas-fired, dry-process kilns typically produce almost three times more NO_x than the coal-fired, dry-process kilns.[7] This fact indicates the dominance of thermal NO in overall NO formation.

3.1.3. Feed NO_x Formation

Similar to coal, the raw materials used in cement production may contain a significant amount of nitrogen. In most cases, limestone is the major raw material, with the remainder of the raw mix being composed of clays, shales, sandstones, sands, and iron ores. Fly ash from coal-fired power plants is used as a raw material and may contain substantial amounts of nitrogen compounds, since it is usually derived from coal. Most of these raw material components are sedimentary minerals and they may contain small amounts of chemically bound nitrogen, presumably of organic origin. Various kiln feeds contain appreciable amounts of nitrogen, ranging from about 20 ppm up to as much as 1,000 ppm (as N).[8] The higher values (>100 ppm) are generally associated with minerals displaying noticeable kerogen contents. Since 100 ppm N in a kiln feed is equivalent to about 1 lb NO_x per ton of clinker (if it all converted), NO_x emissions from the kiln feed may represent a major source of NO_x from cement kilns. Nevertheless, it is probably less important than thermal NO_x and fuel NO_x in most cases.

The same study indicated that conversion of feed nitrogen to NO_x occurs mainly in the 300 to 800°C (570 to 1,470°F) temperature range and depends upon the feed heating rate.[8] Rapid heating rates (~1,000°C flash heating) of the kiln feed mixtures were found to give much lower conversion efficiencies, whereas slow heating rates of kiln feed mixtures (~60°C/min) gave fairly high conversion of about 50 percent of bound nitrogen to NO_x. These results were explained by assuming that the organic nitrogen must vaporize from the sample prior to oxidation if high conversion efficiencies to NO_x are to be achieved. If heating rates are rapid, "cracking" of these volatile compounds may occur in situ, and this may result in conversion of the bound nitrogen directly to N_2 before it comes into contact with gaseous oxygen, thus

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reducing the fraction converted to NO_x. Such a hypothesis is also consistent with the observation that, during coal combustion, the involatile or "char" nitrogen is converted to NO_x much less efficiently than the volatile nitrogen.[9]

3.14. <u>Factors Affecting NO_x Emissions in Cement Manufacturing</u>

There are four primary types of cement kilns used in the industry: wet kilns, long dry kilns, kilns with a preheater, and kilns with a preheater/precalciner. The wet and long dry kilns and some preheater kilns will have only one fuel combustion zone, whereas the newer preheater and precalciner kiln designs have two or three fuel combustion zones: kiln burning zone, riser duct and precalciner. Because the typical temperatures present in the combustion zones are different, the factors affecting NO_x formation are also somewhat different in different kiln types and are discussed in the following sections. In addition to the specific NO_x formation mechanisms, the energy efficiency of the cement-making process is also important as it determines the amount of heat input needed to produce a unit quantity of cement. A high thermal efficiency would lead to less consumption of heat and fuel, and would generally produce lower NO_x emissions.

3.1.4.a. NO_x Formation in the Kiln Burning Zone

In the kiln burning zone, thermal NO_x provides the primary mechanism for NO_x formation. Thermal NO_x formation depends upon the combustion zone temperature, the gasphase residence time and the oxygen concentration in the high temperature combustion zone. The flame temperature strongly depends upon the type of fuel burned. The temperature and intensity are generally greater for gas burners than coal burners. The oxygen concentration in the combustion zone depends upon the overall excess air used and on the source and proportion of primary and secondary combustion air. Less primary air may produce an initial high-temperature, fuel-rich combustion zone followed by a low-temperature fuel-lean combustion zone. Such a combination is likely to reduce NO_x formation.

The firing system used in the kiln affects the proportion of primary and secondary combustion air. Direct firing systems introduce a large proportion of combustion air with the fuel

being burned. This produces two conflicting effects for NO_x emissions: higher oxygen concentration or fuel lean combustion and lower gas temperature. Indirect firing systems on the other hand use only a small portion of combustion air to convey fuel and thus use less primary air. In general, direct fired systems may be expected to produce greater NO_x emissions compared to indirect fired systems. The flame shape and the theoretical flame temperature are important factors in thermal NO_x formation as these factors determine the hottest points in the flame. A long "lazy" flame will produce less NO than a short intense flame.

The flame shape depends on the fuel being burned as well as the proportion of air. For the same amount of primary air, gas burning may be expected to produce a shorter and more intense flame than coal burning. The lower the secondary air temperature and the greater the dust content in the secondary air, the lower the NO_x formation in the kiln burning zone. A large amount of water in the primary air (from a direct firing coal mill) and injection of cement kiln dust (CKD) in the burning zone (insufflation) may also reduce NO_x formation. With increasing excess air percentage, the NO_x formation in the kiln will increase, but only up to a certain point as an increasing excess air rate will reduce the secondary air temperature and, consequently, the flame temperature.

Process conditions that can affect NO_x emissions substantially are: temperature stability, stability of raw mix feed rate, burnability of raw mix, and alkali and sulfur control. Temperature stability is important to maintain the quality of clinker and is achieved by stable-flame conditions and energy efficiency. Clinker formation reactions require temperatures of 2,650 to 2,800°F (1,450 to 1,40°C)[10] and an oxidizing environment. Sometimes natural gas or liquid waste derived fuel is used to control flame conditions and improve clinker quality. The excess air used during combustion has a substantial influence on NO_x emissions. Oxygen levels of 4 to 5 percent in kiln exhaust gases would correspond to high NO_x emissions, whereas oxygen levels of only 0.5 to 1.5 percent would mean lower NO_x emissions. Thus, NO_x emissions in a kiln may depend upon the care exercised by the operator in minimizing excess oxygen needed to maintain the quality of the clinker produced. All but one of the clinker formation reactions are exothermic and represent a dynamic process that requires constant operator adjustments which can vary NO_x formation. .

The heating value of the fuel burned may also affect NO_x emissions. High heating value fuels, such as petroleum coke, require less combustion air and produce less NO_x per ton of clinker.

Different raw material compositions require different burning conditions to maintain the quality of clinker produced. Thus, similar types of kilns with different feed materials may produce different levels of NO_x emissions. The alkali content of finished cement needs to be below a certain acceptable level. Low alkali requirements may require higher kiln temperatures and longer residence times at high temperatures to volatilize the alkali present in the molten clinker. Raw materials with greater alkali content may need to be burned longer at higher temperatures to meet alkali requirements and thus may produce greater NO_x emissions. Increased volatilization of alkali results in increased alkali emissions in kiln exhaust gases. To control alkali emissions, a part of the kiln exhaust gases may be bypassed around a downstream unit, e.g., a precalciner. The bypassed gases are quenched to remove alkali and sent through a particulate matter collector. This alkali-rich particulate matter is removed from the process and disposed. The bypass of kiln exhaust gases typically involves a fuel penalty, e.g., about 20,000 Btu/ton of clinker for every 1 percent gas bypass. The additional heat requirement will contribute to increased NO_x emissions.

Wet kilns require about 33 percent more thermal energy than a dry kiln. This means a greater volume of exhaust gas from a wet kiln for the same production. On the other hand, the greater amount of combustion air will also mean a somewhat lower secondary air temperature. Based on these contradicting factors, one might expect the NO_x emissions from a wet process kiln to be similar to the dry and preheater kilns without riser duct firing.

3.1.4.b. NO_x Formation in Secondary Firing

In the secondary firing region of precalcining kilns, where temperatures range from 820 to 1100°C (1500 to 2000°F), the following reactions may take place:

$$"N" + O \rightarrow NO \qquad (4\text{-}3)$$
$$"N" + NO \rightarrow N2 + O \qquad (4\text{-}4)$$
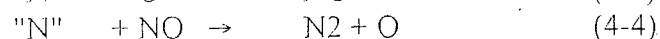
where "N" means nitrogen originating from nitrogen compounds in the fuel.[1] Reaction (4-3) shows that NO formation in the secondary firing zone will depend upon the nitrogen content in the fuel and the oxygen level in the firing zone. Reaction (4-4) indicates that, if there is already NO present in the gas introduced into the secondary firing zone, a reduction of this NO may occur with the fuel nitrogen compounds acting as reducing agents. Accordingly, the net formation of NO in the secondary firing zone will also depend upon the initial NO concentration

in the combustion gas. Finally, measurements have shown that the volatile content in the solid fuel and the temperature in the secondary firing zone also influence the NO formation in the secondary firing zone.[11] With increased volatile content in the fuel, the ratio of fuel nitrogen conversion into NO seems to decrease and, as the reaction rate of reaction (4-4) increases more rapidly with the temperature than that of reaction (4-3), an increase in the temperature of the secondary firing region may reduce the net NO formation.[1]

3.1.5. Suspension Preheater (SP) Kilns with Riser Duct Firing.

In many SP kiln systems 10 to 20 percent of the fuel is fired into the riser duct. The preheater systems are more energy efficient compared to long dry kilns. The increased energy efficiency and the reduction in the amount of fuel burned at the higher clinker burning temperature may be expected to reduce the NO_x emissions from preheater kilns when compared with the long dry and wet kilns. Measurements at several riser-duct fired kiln systems indicate that firing coarse fuel (e.g., tires) into the kiln riser duct will reduce NO_x emissions from the kiln systems.[12] This may be explained by the fact that a large part of the fuel falls directly down into the kiln charge, creating a reducing atmosphere in the kiln back-end where NO_x from the burning zone is reduced.

Conversely, when firing finely ground fuel into the kiln riser duct, the NO_x content in the exhaust gas may increase on passing through the riser duct. As the NO_x emissions from the kiln may also increase slightly due to an increased excess air rate, the total NO_x emissions from the kiln system may increase when starting up riser duct firing with finely ground fuel.[1]

3.1.6. Precalcining Kiln Systems.

In precalcining kiln systems with a tertiary air duct, firing into the rotary kiln typically accounts for only 40 to 50 percent of the total heat consumption and the specific amount of combustion gases from the kiln burning zone is reduced proportionally. Precalciner kilns also typically require the least amount of energy per unit amount of clinker produced. The lower energy requirement and the substantial reduction in the proportion of the fuel burned at clinker burning temperatures may be expected to reduce the NO_x emissions from the precalciner kilns as compared to the preheater kilns. On the other hand, the NO_x concentration (in ppm) in the kiln

gas may be considerably higher than in preheater kilns. This is probably due to the shorter material and longer gas retention times in the precalciner kiln burning zone combined with a very high secondary air temperature.[1]

When examining the contribution from the calciner firing to the emission of NO_x, two basically different types of precalcining kiln systems need to be considered:

- • The in-line (ILC) type in which the kiln gas passes through the firing region of the precalciner, and

- • The separate line (SLC) type in which the kiln exhaust gas bypasses the firing region of the precalciner.

ILC systems: In these systems, the fuel combustion in the calciner takes place in a mixture of the kiln exhaust gas and hot air from the cooler (tertiary air). Some of the nitrogen in the fuel reacts with NO from the kiln exhaust gas while another part reacts with oxygen to form NO. The result may be a net increase or a net reduction of NO in the calciner.

SLC systems: In these systems, the fuel combustion in the calciner takes place in pure hot air. In the case of oil firing, NO production in the calciner is negligible; but when using fuels containing fuel-bound nitrogen, up to 50 percent of the nitrogen compounds in the fuel may be converted into NO_x. The specific NO_x, production in an SLC calciner may be as high as 4 lb NO_x per ton of clinker as measured in a calciner fired with petroleum coke which has a high nitrogen content and low volatile content.[1] The NO_x in the calciner exhaust gas is added to the NO_x in the gas from the rotary kiln which leaves this type of kiln system without being reduced. When fired with solid fuels, SLC systems may therefore be expected to generate somewhat higher NO_x emissions than the ILC systems.[1] We should note, however, that some of the oxygen for combustion of the fuel in ILC systems passes through the burning zone, so the NO generated there may be higher (or lower due to lower temperatures) than for SLC systems.

3.1.7. Energy Efficiency of the Cement-Making Process

Since NO_x formation is directly related to fuel combustion, any reduction in the amount of fuel burned per unit amount of clinker produced should reduce NO_x emissions per unit clinker. Attempts to improve energy efficiency of the process by avoiding excessive clinker burning and

utilizing waste heat effectively for preheating combustion air, coal, and raw mix is likely to reduce NO_x emissions. Improving heat transfer between hot gases and solid materials, e.g., by chain systems, will improve energy efficiency. The newer preheater and precalciner kiln designs provide very efficient preheating and precalcining of the raw mix with intimate gassolids contact in cyclone towers. New cement kiln installations or renovations of older kilns thus predominantly involve precalciner designs for their energy efficiency. The inherent energy efficiency of these kiln designs is likely to produce lower NO_x emissions per unit amount of clinker as compared to the wet or long dry kilns.